

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

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OFFICE OF WATER

MEMORANDUM

SUBJECT: Comparison of Variability Between WET Methods and Chemical Methods

Approved at 40 CFR Part 136

FROM: Marion Kelly, Engineering and Analysis Division, Office of Science and

Technology

TO: File

EPA compared the precision of WET test methods (as measured in the WET Interlaboratory Variability Study) to chemical methods approved at 40 CFR Part 136 using regression equations published for these methods in Appendices A and D of 40 CFR Part 136. The details of this analysis and the data included in the analysis are presented in Attachment A of this memo. This analysis concluded that the precision of WET test methods is within the range of precision observed for chemical methods approved at 40 CFR Part 136. The median interlaboratory variability (CV) for chemical methods is 17% for metals analysis and 28% for organics analysis (Table 1). The median CV for the 10 WET methods ratified in the WET rulemaking is 32%. While the median variability is lower for chemical methods than WET methods, the range of variability exhibited by chemical methods is wider than and encompasses the variability range exhibited by WET methods. The variability of individual chemical methods depends on the method and the analyte being measured. Some analytes can be measured very precisely, such as copper by Method 200.7 (CV of 7), and some analytes are measured with less precision, such as DDT by Method 625 (CV of 64). Chemical methods for the analysis of metals ranged in interlaboratory variability from 3 to 64%; chemical methods for the analysis of organics ranged in interlaboratory variability from 12 to 104%. The range of interlaboratory variability for WET methods was 11 to 44%, which is well within the range for both metals and organics analysis.

Table 1. Comparison of interlaboratory variability (CVs) between WET methods and chemical methods.

	Chemical Methods for the Analysis of Metals	Chemical Methods for the Analysis of Organics	WET methods
N .	52	211	10
Median CV	17	28	32
Range of CVs	3-64	12-104	11-44
Percentiles of CVs			
10%	7	18	19
25%	10	22	22
50%	17	28	32
75%	26	40	38
90%	39	53	42

Attachment A: Supporting Data and Analysis

In Appendices A and D of 40 CFR Part 136, method precision is described for a number of methods and analytes. Method precision is described by a regression equation relating overall interlaboratory precision (measured as a standard deviation) to the measured concentration of the analyte. Such equations are provided because precision generally decreases as the concentration of the analyte approaches the limit of detection for the method. For each of the methods and analytes listed in these appendices (with the exception of isotope dilution methods), an interlaboratory CV was calculated based on the regression equation: (concentration x slope + intercept) / concentration x 100%. The CVs were calculated using the concentration at the center (on a log scale) of the concentration range used to establish each regression equation. Table 2 lists the regression parameters, evaluated concentration, and calculated interlaboratory CV for each of these methods and analytes. Table 3 lists the interlaboratory variability measured for the WET methods in EPA's WET Interlaboratory Variability Study for comparison.

Table 2. Regression equations and interlaboratory variability (CV) for methods listed in 40

CFR Part 136 Appendix A and D.

Method	Parameter	Evaluated concentration (ug/L)	Slope	Intercept	CV (%)
200.7	Aluminum	575	0.0559	18.6	9
200.7	Antimony	329	0.1556	-0.6	15
200.7	Arsenic	361	0.1239	2.4	13
200.7	Barium	58	0.1819	2.78	23
200.7	Beryllium	76	0.0136	0.95	3
200.7	Boron	314	0.115	14.1	16
200.7	Cadmium	132	0.557	2.02	57
200.7	Calcium	895	0.1228	10.1	13
200.7	Chromium	135	0.0499	4.4	8
200.7	Cobalt	199	0.0436	3.8	6
200.7	Copper	123	0.0442	2.85	7
200.7	Iron	349	0.0683	11.5	10
200.7	Lead	445	0.0558	7	7
200.7	Magnesium	687	0.0607	11.6	8
200.7	Manganese	87	0.0324	0.88	4
200.7	Molybdenum	176	0.0618	1.6	7
200.7	Nickel	895	0.0604	4.4	7
200.7	Potassium	2216	0.0934	77.8	13
200.7	Selenium	312	0.0855	17.8	14
200.7	Silicon	1335	0.416	37.8	44
200.7	Silver	39	0.5055	-3.05	43
200.7	Sodium	1285	0.2097	33	24
200.7	Thallium	337	0.1004	18.3	15
200.7	Vanadium	247	0.0618	1.7	7

		Evaluated			CV
Method	Parameter	concentration	Slope	Intercept	(%)
200.7	771	(ug/L)	0.0014	2.75	11
200.7	Zinc	223	0.0914	3.75	23
202.1	Aluminum	775	0.066	125	41
202.2	Aluminum	50	0.4286 0.3732	-0.124 0.854	39
204.2	Antimony				· · · · · · · · · · · · · · · · · · ·
206.2	Arsenic	48	0.1411	1.873	18
206.4	Arsenic	76	0.198	5.93	28
208.2	Barium	157	0.2466	6.436	29
210.2	Beryllium	2	0.2167	0.09	26.
213.1	Cadmium	33	0.108	5.08	26
213.2	Cadmium	2	0.23	0.045	25
218.1	Chromium	174	0.131	4.26	16
218.2	Chromium	49	0.1684	0.852	19
219.2	Cobalt	99	0.2481	-2.541	22
220.1	Copper	141	0.047	12.3	13
220.2	Copper	9.	0.2735	-0.058	27
236.1	Iron	542	0.022	41	10
236.2	Iron	13	0.3611	-0.079	36
239.1	Lead	176	0.028	33.9	22
239.2	Lead	51	0.2224	0.507	23
243.1	Manganese	198	0.042	8.95	9
243.2	Manganese	17	0.2001	1.042	26
249.2	Nickel	112	0.2475	1.896	26
270.2	Selenium	50	0.1584	0.878	18
272.2	Silver	5.	0.1805	0.153	21
279.2	Thallium	50	0.1112	0.669	12
286.2	Vanadium	37	0.3323	-0.428	32
289.1	Zinc	132	0.078	10.8	16
289.2	Zinc	10	0.674	-0.342	64
601	1,1,1-Trichloroethane	63	0.2	0.37	21
601	1,1,2,2-Tetrachloroethene	63	0.23	2.79	27
601	1,1,2-Trichloroethane	63	0.19	0.67	20
601	1,1-Dichloroethane	63	0.14	0.94	15
601	1,1-Dichloroethene	63	0.29	-0.4	28
601	1,2-Dichlorobenzene	63	0.13	6.13	23
601	1,2-Dichloroethane	63	0.15	0.94	16
601	1,2-Dichloropropane	63	0.23	0	23
601	1,3-Dichlorobenzene	63	0.26	2.34	30
601	1,4-Dichlorobenzene	63	0.2	0.41	21
601	2-Chloroethylvinyl ether	63	0.35	0	35
601	Bromodichloromethane	63	0.2	1	22
601	Bromoform	63	0.21	2.41	25

Method	Parameter	Evaluated concentration (ug/L)	Slope	Intercept	CV (%)
601	Bromomethane	63	0.36	0.94	37
601	Carbon tetrachloride	63	0.2	0.39	21
601	Chlorobenzene	63	0.18	1.21	20
601	Chloroethane	63	0.17	0.63	18
601	Chloroform	63	0.19	-0.02	19
601	Chloromethane	63	0.52	1.31	54
601	cis-1,3-Dichloropropene	63	0.32	0	32
601	Dibromochloromethane	63	0.24	1.68	27
601	Methylene chloride	63	0.21	1.43	23
601	Tetrachloroethene	63	0.18	2.21	21
601	trans-1,2-Dichloroethene	63	0.17	1.46	19
601	trans-1,3-Dichloropropene	63	0.32	0	. 32
601	Trichloroethene	63	0.23	0.3	23
601	Trichlorofluoromethane	63	0.26	0.91	27
601	Vinyl chloride	63	0.27	0.4	28
602	1,2-Dichlorobenzene	34	0.22	0.53	24
602	1,3-Dichlorobenzene	34	0.19	0.09	19
602	1,4-Dichlorobenzene	34	0.2	0.41	21
602	Benzene	34	0.21	0.56	23
602	Chlorobenzene	34	0.17	0.1	17
602	Ethylbenzene	34	0.26	0.23	27
602	Toluene	34	0.18	0.71	20
604	2,4,6-Trichlorophenol	73	0.13	2.4	16
604	2,4-Dichlorophenol	73	0.18	0.62	19
604	2,4-Dimethylphenol	73	0.25	0.48	26
604	2,4-Dinitrophenol	73	0.29	4.51	35
604	2-Chlorophenol	73	0.21	0.75	22
604	2-Nitrophenol	73	0.14	3.84	19
604	4,6-Dinitro-2-methylphenol	73	0.19	5.85	27
604	4-Chiloro-3-methylphenol	73	0.16	1.41	18
604	4-Nitrophenol	73	0.19	4.79	26
604	Pentachlorophenol	73	0.23	0.57	24
604	Phenol	73	0.17	0.77	1/8
605	3,3'-Dichlorobenzidine	8	0.38	0.02	38
605	Benzidine	8	0.4	0.18	42
606	Bis(2-ethylhexyl) phthalate	9	0.73	-0.17	71
606	Butyl benzyl phthalate	9	0.25	0.07	26
606	Diethyl phthalate	9	0.45	0.11	46
606	Dimethyl phthalate	9	0.44	0.31	48
606	Di-n-butyl phthalate	9	0.29	0.06	30
606	Di-n-octyl phthalate	9	0.62	0.34	66

Method	Parameter	Evaluated concentration (ug/L)	Slope	Intercept	CV (%)
607	N-nitrosodimethylamine	7	0.25	0.11	27
607	N-nitrosodi-n-propylamine	7	0.21	0.15	23
607	N-nitrosodiphenylamine	7	0.46	-0.47	39
608	4,4'-DDD	4	0.27	-0.14	23
608	4,4'-DDE	4	0.28	-0.09	26
608	4,4'-DDT	4	0.31	-0.21	26
608	α-ВНС	4	0.23	0	· 23
608	Aldrin	4	0.2	-0.01	20
608	β-ВНС	4	0.33	-0.05	32
608	Chlordane	58	0.18	0.18	18
608	Dieldrin	4	0.16	0.16	20
608	Endosulfan I	4	0.18	0.08	20
608	Endosulfan II	4	0.47	-0.2	42
608	Endosulfan sulfate	4	0.24	0.35	33
608	Endrin	4	0.24	0.25	30
608	у-ВНС	4	0.22	0.04	23
608	Heptachlor	4	0.16	0.08	18
608	Heptachlor epoxide	4	0.25	-0.08	23
608	PCB-1016	58	0.15	0.45	16
608	PCB-1221	58	0.35	-0.62	34
608	PCB-1232	58	0.31	3.5	37
608	PCB-1242	58	0.21	1.52	24
608	PCB-1248	58	0.25	-0.37	24
608	PCB-1254	58	0.17	3.62	23
608	PCB-1260	58	0.39	-4.86	3,1
608	δ-ВНС	4	0.25	0.03	26
608	Toxaphene	58	0.2	0.22	20
609	2,4-Dinitrotoluene	23	0.37	-0.07	37
609	2,6-Dinitrotoluene	23	0.36	0	36
609	Isophorone	23	0.46	0.31	47
609	Nitrobenzene	23	0.37	-0.78	34
610	Acenaphthene	. 7	0.53	1.32	73
610	Acenaphthylene	7	0.42	0.52	50
610	Anthracene	, 7	0.41	0.45	48
610	Benzo(k)fluoranthene	7	0.69	0.01	69
610	Benzo(a)anthracene	7	0.34	0.02	34
610	Benzo(a)pyrene	7	0.53	-0.01	53
610	Benzo(b)fluoranthene	7	0.38	0	38
610	Benzo(ghi)perylene	7	0.58	0.1	60
610	Chrysene	7	0.66	-0.22	63
610	Dibenzo(a,h)anthracene	7	0.45	0.03	45

Method	Parameter	Evaluated concentration	Slope	Intercept	cv
Michiga	Tarameter	(ug/L)	Slope	Пистесрі	(%)
610	Fluoranthene	7	0.32	0.03	32
610	Fluorene	7	0.63	-0.65	53
610	Indeno(1,2,3-cd)pyrene	7	0.42	0.01	42
610	Naphthalene	7	0.41	0.74	52
610	Phenanthrene	7	0.47	-0.25	43
610	Pyrene	7	0.42	0	42
611	4-Bromophenyl phenyl ether	25	0.47	0.37	48
611	4-Chlorophenyl phenyl ether	25	0.41	0.55	43
611	Bis(2-chloroethoxy) methane	25	0.33	0.11	33
611	Bis(2-chloroethyl) ether	25	0.35	0.36	36
611	Bis(2-chloroisopropyl) ether	25	0.36	0.79	39
612	1,2,4-Trichlorobenzene	19	0.4	-1.37	33
612	1,2-Dichlorobenzene	19	0.41	-3.92	20
612	1,3-Dichlorobenzene	19	0.49	-3.98	28
612	1,4-Dichlorobenzene	19	0.35	-0.57	32
612	2-Chloronaphthalene	- 19	0.38	-1.39	31
612	Hexachlorobenzene	19	0.36	-0.19	35
612	Hexachlorobutadiene	19	0.53	-0.12	52
612	Hexachlorocyclopentadiene	19	0.5	0	50
612	Hexachloroethane	19	0.36	0.	36
613	2,3,7,8-TCDD	0.06	0.19	0.00028	19
624	1,1,1-Trichloroethane	55	0.21	-0.39	20
624	1,1,2,2-Tetrachloroethene	55	0.2	0.41	21
624	1,1,2-Trichloroethane	55	0.18	0	18
624	1,1-Dichloroethane	55	0.16	0.47	17
624	1,1-Dichloroethene	55	0.43	-0.22	43
624	1,2-Dichlorobenzene	55	0.3	-1.2	28
624	1,2-Dichloroethane	55	0.21	-0.38	20
624	1,2-Dichloropropane	55	0.45	0	45
624	1,3-Dichlorobenzene	55	0.18	-0.82	17
624	1,4-Dichlorobenzene	55	0.3	-1.2	28
624	2-Chloroethylvinyl ether	55	0.84	0	84
624	Benzene	55	0.25	-1.33	23
624	Bromodichloromethane	55	0.2	1.13	22
624	Bromoform	55	0.17	1.38	20
624	Bromomethane	55	0.58	0	58
624	Carbon tetrachloride	55	0.11	0.37	12
624	Chlorobenzene	55	0.26	-1.92	22
624	Chloroethane	55	0.29	1.75	32
624	Chloroform	55	0.18	0.16	18
624	Chloromethane	55	0.58	0.43	59

Method	Parameter	Evaluated concentration	Slope	Intercept	CV
Method	i arameter	(ug/L)	Slope	Intercept	(%)
624	cis-1,3-Dichloropropene	55	0.52	0	52
624	Dibromochloromethane	55	0.17	0.49	18
624	Ethylbenzene	55	0.26	-1.72	23
624	Methylene chloride	55	0.32	4	39
624	Tetrachloroethene	55	0.16	-0.45	15
624	Toluene	55	0.22	-1.71	19
624	trans-1,2-Dichloroethene	55	0.19	0.17	19
624	trans-1,3-Dichloropropene	55	0.34	0	34
624	Trichloroethene	55	0.12	0.59	13
624	Trichlorofluoromethane	55	0.34	-0.39	33
624	Vinyl chloride	55	0.65	0	65
625	1,2,4-Trichlorobenzene	81	0.21	0.39	21
625	1,2-Dichlorobenzene	81	0.24	0.39	24
625	1,3-Dichlorobenzene	81	0.41	0.11	41
625	1,4-Dichlorobenzene	81	0.29	0.36	29
625	2,4,6-Trichlorophenol	8.1	0.22	1.81	24
625	2,4-Dichlorophenol	81	0.21	1.28	23
625	2,4-Dimethylphenol	81	0.22	1.31	24
625	2,4-Dinitrophenol	81	0.42	26.29	75
625	2,4-Dinitrotoluene	81	0.21	1.5	23
625	2,6-Dinitrotoluene	81	0.19	0.35	19
625	2-Chloronaphthalene	81	0.13	0.34	13
625	2-Chlorophenol	81	0.28	0.97	29
625	2-Methyl-4,6-dinitrophenol	81	0.26	23.1	55
625	2-Nitrophenol	81	0.27	2.6	30
625	3,3'-Dichlorobenzidine	81	0.47	3.45	51
625	4,4'-DDD	81	0.66	-0.96	- 65
625	4,4'-DDE	81	0.39	-1.04	38
625	4,4'-DDT	81	0.65	-0.58	64
625 625 625	4-Bromophenyl phenyl ether	81	0.16	0.66	17
625	4-Chloro-3-methylphenol	81	0.29	1.31	31
625	4-Chlorophenyl phenyl ether	81	0.3	-0.46	29
625	4-Nitrophenol	81	0.44	3.24	48
625	Acenaphthene	81	0.21	-0.67	20
625	Acenaphthylene	81	0.26	-0.54	25
625 625 625	Aldrin	81	0.43	1.13	44
625	Anthracene	81	0,27	-0.64	26
625	β- В НС	81	0.3	-1.94	28
625	Benzo(a)anthracene	81	0.26	-0.28	26
625	Benzo(a)pyrene	81	0.32	1.35	34
625	Benzo(b)fluoranthene	81	0.29	0.96	30

Method	Parameter	Evaluated concentration (ug/L)	Slope	Intercept	CV (%)
625	Benzo(ghi)perylene	81	0.51	-0.44	50
625	Benzo(k)fluoranthene	81	0.35	0.4	35
625	Benzyl butyl phthalate	81	0.53	0.92	54
625	Bis(2-chloroehtyl) ether	81	0.35	0.1	35
625	Bis(2-chloroethoxy) methane	81	0.26	2.01	28
625	Bis(2-chloroisopropyl) ether	81	0.25	1.04	26
625	Bis(2-ethylhexyl) phthalate	81	0:36	0.67	37
625	Chrysene	81	0.33	-0.09	33
625	Dibenzo(a,h)anthracene	81	0.59	0.25	59
625	Dieldrin	81	0.26	-0.07	26
625	Diethyl phthalate	81	0.52	0.22	52
625	Dimethyl phthalate	81	1.05	-0.92	104
625	Di-n-butyl phthalate	81	0.39	0.6	40
625	Di-n-octyl phthalate	81	0.37	1.19	38
625	Endosulfan sulfate	81	0.63	-1.03	62
625	Endrin aldehyde	81	0.73	-0.62	72
625	Fluoranthene	81	0.28	-0.6	27
625	Fluorene	81	0.13	0.61	14
625	Heptachlor	81	0.5	-0.23	50
625	Heptachlor epoxide	81	0.28	0.64	29
625	Hexachlorobenzene	81	0.43	-0.52	42
625	Hexachlorobutadiene	81	0.26	0.49	27
625	Hexachloroethane	81	0.17	0.8	18
625	Indeno(1,2,3-cd)pyrene	81	0.5	0.44	51
625	Isophorone	81	0.33	0.26	33
625	Naphthalene	81	0.3	-0.68	29
625	Nitrobenzene	81	0.27	0.21	27
625	N-nitrosodi-n-propylamine	81	0.44	0.47	45
625	PCB-1260	81	0.43	1.82	45
625	Pentachlorophenol	81	0.3	4.33	35
625	Phenanthrene	81	0.15	0.25	15
625	Phenol	81	0.35	0.58	36
625	Pyrene	81	0.15	0.31	15
625	8-BHC	81	0.93	-0.17	93

Table 3. Interlaboratory variability (CV) of WET methods.

Method	CV (%)
Ceriodaphnia dubia Acute Test	29.0
Ceriodaphnia dubia Survival and Reproduction Test	35.0
Fathead Minnow Acute Test	20.0
Fathead Minnow Larval Survival and Growth Test	20.9
Selenastrum capricornutum Growth Test	34.3
Mysidopsis bahia Survival, Growth, and Fecundity Test	41.3
Sheepshead Minnow Acute Test	26.0
Sheepshead Minnow Larval Survival and Growth Test	10.5
Menidia beryllina Acute Test	38.5
Menidia beryllina Larval Survival and Growth Test	43.8